

Static magnetic order of $\text{Sr}_4\text{A}_2\text{O}_6\text{Fe}_2\text{As}_2$ ($\text{A} = \text{Sc}$ and V) revealed by local probes

J. Munevar,¹ D. R. Sánchez,^{2,1} M. Alzamora,¹ E. Baggio-Saitovitch,¹ J. P. Carlo,³ T. Goko,^{3,4}
A. A. Aczel,⁵ T. J. Williams,⁵ G. M. Luke,^{5,6} Hai-Hu Wen,⁷ Xiyu Zhu,⁷ Fei Han,⁷ and Y. J. Uemura^{3,*}

¹*Centro Brasileiro de Pesquisas Físicas, Rua Xavier Sigaud 150, Rio de Janeiro, Brazil*

²*Instituto de Física, Universidade Federal Fluminense, 24210-346 Niterói, RJ, Brazil*

³*Department of Physics, Columbia University, New York, New York 10027, USA*

⁴*TRIUMF, 4004 Wesbrook Mall, Vancouver, B.C., V6T 2A3, Canada*

⁵*Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

⁶*Canadian Institute of Advanced Research, Toronto, Ontario M5G 1Z8, Canada*

⁷*National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, People's Republic of China*

(Dated: November 9, 2010)

Static magnetic order of quasi two-dimensional FeAs compounds $\text{Sr}_4\text{A}_2\text{O}_{6-x}\text{Fe}_2\text{As}_2$, with $\text{A} = \text{Sc}$ and V , has been detected by ^{57}Fe Mössbauer and muon spin relaxation (μSR) spectroscopies. The non-superconducting stoichiometric ($x = 0$) $\text{A} = \text{Sc}$ system exhibits a static internal/hyperfine magnetic field both at the ^{57}Fe and μ^+ sites, indicating antiferromagnetic order of Fe moments below $T_N = 35$ K with ~ 0.1 Bohr magneton per Fe at $T = 2$ K. The superconducting and oxygen deficient ($x = 0.4$) $\text{A} = \text{V}$ system exhibits a static internal field only at the μ^+ site below $T_N \sim 40$ K, indicating static magnetic order of V moments co-existing with superconductivity without freezing of Fe moments. These results suggest that the 42622 FeAs systems belong to the same paradigm with the 1111 and 122 FeAs systems with respect to magnetic behavior of Fe moments.

PACS numbers: 74.70.Xa 75.30.-m 76.80.+y 76.75.+i

Since the discovery in the spring of 2008 [1], iron arsenide superconductors and related systems have generated a burst of research. These compounds have a FeAs layer together with a charge reservoir layer composed of RO (with R as a rare earth) in the “1111” systems [1–5], alkali atoms (Ca, Sr, Ba) in the “122” materials [6–8], and Li and Na atoms in the “111” compounds [9, 10]. In the 1111, 122, and Na-based 111 FeAs compounds, parent systems exhibit antiferromagnetic order, and superconductivity arises through carrier doping via chemical substitutions and/or application of external pressure. Recently, several groups reported synthesis of a new group of FeAs systems separated by perovskite layers such as Sr_2AO_3 , leading to the “42622” systems $\text{Sr}_4\text{A}_2\text{O}_{6-x}\text{Fe}_2\text{As}_2$ [11–14], where A denotes Sc, Ti, Cr, V, and other transition metal atoms. Subsequently discovered were “32522” $\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$ [15], the homologous series of $\text{Ca}_{n+1}\text{M}_n\text{O}_y(\text{Fe}_2\text{As}_2)$ [$n = 3, 4, 5$, $y \sim 3n-1$, $\text{M} = (\text{Sc}, \text{Ti})$ and (Mg, Ti)] [16], and $(\text{Ca}_{n+2}(\text{Al}, \text{Ti})_n\text{O}_y)(\text{Fe}_2\text{As}_2)$ [$n = 2, 3, 4$] [17]. Despite a large distance between FeAs layers separated by the perovskite layers, many of these “perovskite + FeAs” (perov-FeAs) systems exhibit superconductivity, with the T_c reaching as high as 47 K [16].

Study of magnetic order of perov-FeAs systems, however, has been difficult, because: (1) non-superconducting compounds do not exhibit clear signature of the spin density wave (SDW) ordering of Fe in resistivity nor crystal structure, most-likely due to weak magnetic coupling between FeAs layers separated by a larger interplane distance; (2) it is often difficult to separate magnetism of Fe from that of V, Cr, and

other transition-metal elements in these systems; and (3) neutron scattering and magnetization measurements do not provide information on the volume fraction of magnetically ordered regions. No signature of static order of Fe was detected by the ^{57}Fe Mössbauer effect in $\text{Ba}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$ [18] and $\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$ [15], and magnetic order of Fe has so far not been reported in any of the perov-FeAs systems to our knowledge. Static magnetic order of the transition metal atom A in $\text{Sr}_4\text{A}_2\text{O}_6\text{Fe}_2\text{As}_2$ ($\text{A} = \text{Cr}, \text{V}$) was reported from neutron scattering [14, 19] and the ^{57}Fe Mössbauer effect [18] for the $\text{A} = \text{Cr}$ compound, and from X-ray absorption and Mössbauer [20] measurements for the $\text{A} = \text{V}$ compound. The results on the $\text{A} = \text{V}$ compound, however, are not conclusive due to limited neutron signal quality on polycrystalline specimens in ref. [19], and limited temperature range ($T > 20$ K), indirect signature relying on the absence of Fe ordering, and lack of volume-related information in ref. [20].

In this paper, we present a combination of ^{57}Fe Mössbauer effect and positive muon spin relaxation ($\mu^+\text{SR}$) measurements, which clearly reveal that: (a) non-superconducting $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$ exhibits antiferromagnetic SDW order of Fe moments; (b) superconducting $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ exhibits static magnetic order of V moments (without ordering of Fe sub-lattice), coexisting with superconductivity; and (c) magnetic order in both of these systems develops in the full volume fraction.

Polycrystalline sintered specimens of stoichiometric $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$ and oxygen deficient $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (samples # 1 - # 3) were synthesized in Beijing following the methods described in refs. [12, 13]. The $\text{A} = \text{V}$ sam-

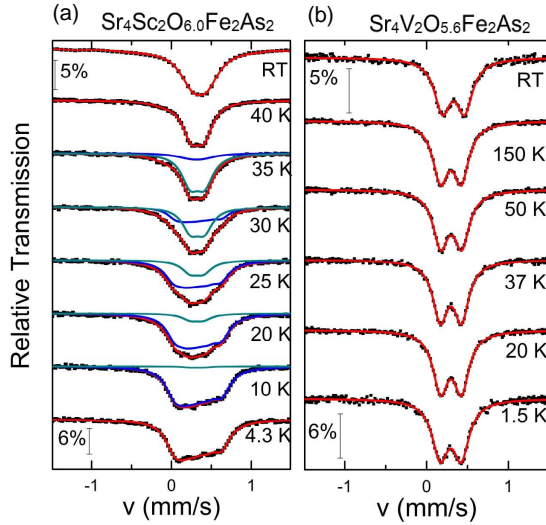


FIG. 1: ^{57}Fe Mössbauer effect spectra in (a) non-superconducting $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$, and (b) superconducting $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (# 3). The spectra in (a) have been fitted as a sum of the doublet signal from the paramagnetic Fe (light blue line) and the sextet signal from the ordered static Fe moments (dark blue line). The line width in (b) is nearly independent of temperature for $T = 20 - 300$ K.

ple was checked by magnetization measurements, which confirmed superconductivity below $T \sim 25$ K (Figs. 3(c) and 4(e)) and hysteresis corresponding to a very weak ferromagnetic polarization (Fig. 2(c)) at $T = 5$ K. ^{57}Fe Mössbauer effect and μSR measurements were carried out, respectively, at CBPF (Rio, Brazil) and TRIUMF (Vancouver, Canada) using the same specimens.

Figure 1 compares Mössbauer spectra obtained in the $A = \text{Sc}$ and $A = \text{V}$ compounds. At room temperature, the $A = \text{Sc}$ system shows a unique doublet with the quadrupole splitting value $\Delta E_Q = -0.165(5)$, indicating a single paramagnetic site. As the sample is cooled down below 40 K the doublet splits in two phases, a remaining paramagnetic doublet and a magnetic sextet, indicated by the light-blue and dark-blue lines, respectively, in Fig. 1(a). At $T = 4.3$ K, the paramagnetic signal disappears and the hyperfine field for the magnetic site becomes $1.73(2)$ T, which corresponds to a static Fe moment of $0.12(1) \mu_B$. The angle θ of the moment direction fits to ~ 80 degrees, indicating that the Fe moments align almost perpendicular to the crystallographic c axis. The isomer shift values $\delta = 0.465(3)$ mm/s at $T = 300$ K and $0.426(4)$ mm/s at $T = 4.3$ K indicate that the valence state and electronic configuration surrounding an Fe atom are nearly independent of temperature. Figures 2(a) and (b) show the hyperfine field and the volume fraction of the magnetically ordered region, derived by fitting the sextet signal in the $A = \text{Sc}$ compound.

Figure 1(b) shows the Mössbauer spectra for $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$, from room temperature down to 1.5

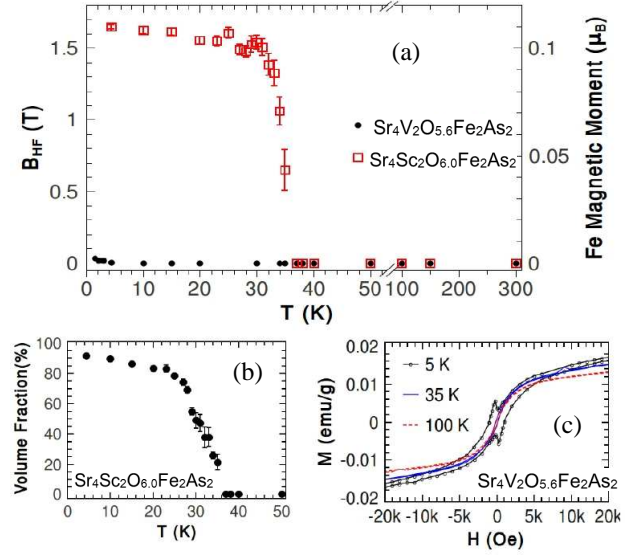


FIG. 2: (a) Static hyperfine field and corresponding Fe moment size in non-superconducting $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$, and superconducting $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (# 3), estimated from the linewidth in ^{57}Fe Mössbauer effect. (b) The volume fraction of ordered Fe in $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$ derived by fitting the spectra as a sum of the doublet line representing paramagnetic Fe and the sextet line for ordered Fe moments. (c) Magnetization hysteresis observed in $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (# 3).

K. The well-defined absorption doublet has an isomer shift $\delta = 0.411(2)$ mm/s and a quadrupole splitting $\Delta E_Q = -0.256(2)$ mm/s typical for low spin Fe^{+2} . These values are nearly independent of temperature, suggesting the absence of structural phase transition, in agreement with previous structural studies [12, 13]. The linewidth exhibits almost no change with decreasing temperature, demonstrating that Fe moments do not participate in static magnetic order in the $A = \text{V}$ 42622 perov-FeAs compound. To estimate the static hyperfine field in this system, we subtracted the linewidth at room temperature from the width observed at low temperatures, and plot the result in Fig. 2(a). This figure clearly demonstrates that the $A = \text{Sc}$ compound exhibits static order of Fe moments, but the $A = \text{V}$ system does not. The linewidth Γ shows a small increase at very lower temperatures: $\Gamma = 0.223(4)$ mm/s at $T = 4.3$ K while $\Gamma = 0.238(7)$ mm/s at $T = 1.5$ K. This could be due to an effective hyperfine field generated by the ordering of V moments. As shown in Fig. 2(c), the $A = \text{V}$ system exhibits hysteresis in the magnetization. This indicates a small ferromagnetic component associated with static ordering of V moments. The observed spontaneous ferromagnetic polarization ~ 0.01 emu/g at $H = 0$ for $T = 5$ K, however, corresponds only to 7×10^{-4} Bohr magneton per V atom.

Figure 3 compares μSR time spectra observed in zero field in the $A = \text{Sc}$ and V compounds. In (a) the Sc

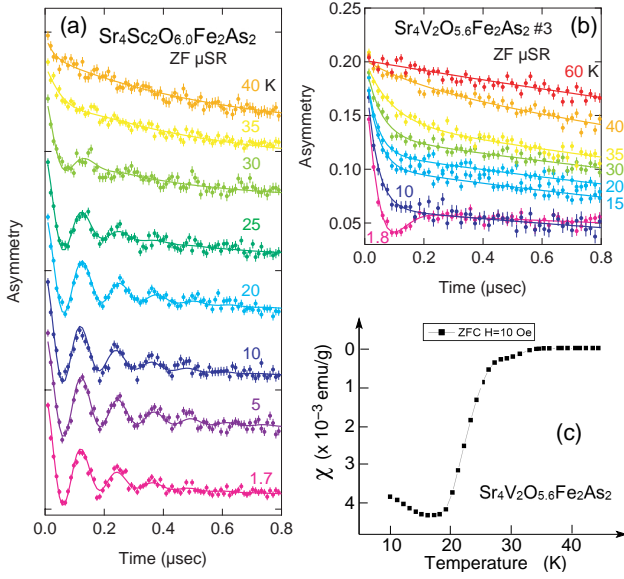


FIG. 3: Time spectra of zero-field μ SR measurements in (a) $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$ and (b) $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (#3). Separate measurements in longitudinal field confirmed that the observed oscillation and relaxation are due to static magnetic fields. (c) shows magnetization results on $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$ (#3), which confirmed the onset of superconductivity at $T \sim 25$ K.

compound exhibits an onset of precession below $T \sim 30$ K, which is a direct indication of static magnetic order. The temperature dependence of the precession frequency $\nu(T)$, shown in Fig. 4(a), is consistent with the results of the Mössbauer hyperfine field in Fig. 2(a). In parent antiferromagnetic compounds of the 122 and 1111 FeAs systems, there exists a nearly linear relationship between the ordering temperature T_N and the ZF- μ SR frequency $\nu(T \rightarrow 0)$ at low temperatures [21], which is proportional to the magnitude of ordered Fe moments. As shown in Fig. 4(b), the results for the $A = \text{Sc}$ 42622 system clearly follow this trend, demonstrating commonalities of Fe magnetism among parent compounds of all of these FeAs systems. The continuous variation of the ordered Fe moment size suggests that this magnetism is likely arising from itinerant Fe electrons, though in some cases localized spin systems exhibit similar behavior due to low dimensionality and/or frustration [22]. The ordered Fe moment size ~ 0.1 Bohr magneton, estimated by μ SR from relative magnitudes of $\nu(T \rightarrow 0)$, is consistent with the Mössbauer results. Figure 4(c) shows the volume fraction of the ordered region estimated by the amplitude of the oscillating μ SR signal. This figure, together with the Mössbauer results in Fig. 2(b), indicate a gradual build up of static magnetic order of Fe moments below $T_N \sim 35$ K in the non-superconducting $A = \text{Sc}$ system.

We also performed μ SR studies on oxygen deficient

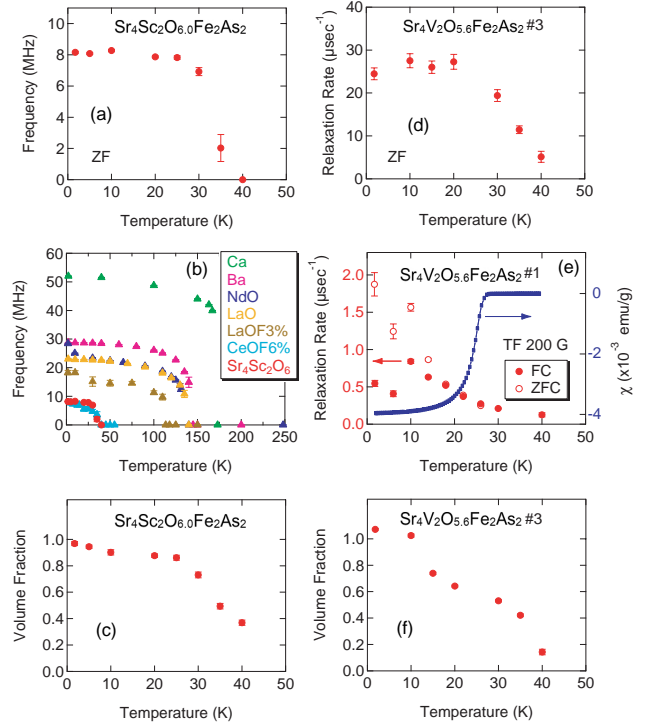


FIG. 4: (a) Muon spin precession frequency in zero field observed in $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$. (b) Comparison of this frequency with those observed in other FeAs systems [21]. (c) Volume fraction of regions with static magnetic order derived from the oscillating amplitude of the μ SR signal in $\text{Sr}_4\text{Sc}_2\text{O}_6\text{Fe}_2\text{As}_2$. (d) Muon spin relaxation rate of the fast-relaxing component in zero field due to static magnetic order, (e) the relaxation rate of the slow-relaxing component from the paramagnetic volume observed in A transverse field of 200 G, and (f) the volume fraction of the magnetically ordered region, in superconducting $\text{Sr}_4\text{V}_2\text{O}_{5.6}\text{Fe}_2\text{As}_2$. The results in (d) and (f) were obtained on sample # 3, while in (e) on sample # 1: both having nominally identical compositions. Magnetic susceptibility of sample # 1 in (e) shows the onset of superconductivity.

specimens of the $A = \text{V}$ compound. Susceptibility results in Fig. 3(c) confirm superconductivity of our specimen # 3 with a decent Meissner signal. The zero-field μ SR time spectra in Fig. 3(b) exhibit the onset of a fast relaxation, causing damping of the asymmetry within $t = 200$ ns, below $T \sim 40$ K. With a separate μ SR study in a longitudinal field, we confirmed that this relaxation is due to static random fields. Figures 4(e) and (g) show the relaxation rate of the fast-relaxing signal and the volume fraction of the magnetically ordered region derived from the amplitude of that signal. By comparing Fig. 3(a) for the $A = \text{Sc}$ system and Fig. 3(b) for the V system, we notice that the rate of initial damping of the asymmetry is comparable. This indicates that the static internal fields at the muon site in these two systems are comparable in magnitude. Although it is not possible to provide a more precise estimate due to lack of information on the

location of the muon site and the exact spin configuration of the V moments, this observation points towards ~ 0.1 Bohr magneton as an order of magnitude estimate for the static V moment at $T \rightarrow 0$. This finding, together with the small magnetic hysteresis loop measured, suggest dominantly antiferromagnetic spin correlations of V moments, consistent with recent neutron measurements [19]. We note that commensurate antiferromagnetic order was observed by neutron scattering in a stoichiometric $A = \text{Cr}$ 42622 perov-FeAs compound with an ordered moment size of 2.75 Bohr magneton per Cr [14].

In the $A = \text{V}$ compound, between $T = 15 - 40$ K, a significant volume fraction remains without having a large internal field from static V moments. In separate μSR measurements in a transverse external field (TF) of 200 G, we attempted to measure the magnetic field penetration depth from the signal representing such “paramagnetic/nonmagnetic” volume fraction. As shown in Fig. 4(e), we found different TF μSR relaxation rates between the field-cooling (FC) and zero-field-cooling (ZFC) procedures, which is a typical response for superconductors relevant to pinning of flux vortices [23]. The scattering of data points below $T = 15$ K in Fig. 4(e) is due to a decreasing “paramagnetic” volume and difficulty in separating the relaxation due to magnetic order from the effect of flux vortices. The FC relaxation rate $\sigma \sim 1\mu\text{s}^{-1}$ at $T \rightarrow 0$ is comparable to the rate observed in superconducting 1111 and 122 FeAs systems [21]. These results indicate that superconductivity survives at least in the volume without static order of V. Although our μSR results do not give direct information on whether or not superconductivity and magnetic order co-exist in the same volume, the decent Meissner signal and essentially full volume fraction of the magnetically ordered region at $T \rightarrow 0$ suggest that static magnetic order in V sublattices may not give any adverse effect on superconductivity in the FeAs layers.

In summary, the combined Mössbauer and μSR measurements demonstrated static magnetic order of the Fe sub-lattice in the $A = \text{Sc}$ compound and the V sub-lattice in the $A = \text{V}$ 42622 FeAs compound. Contrary to some theoretical proposals [24, 25] suggesting that the 42622 systems may be very different from other FeAs systems with respect to magnetism of the Fe sub-lattices and fermi-surface nesting, the present results indicate that the 42622 systems belong to the same paradigm with other FeAs systems, exhibiting static antiferromagnetic order of Fe moments in the parent non-superconducting compound and superconductivity without static order of the Fe sub-lattice in a carrier-doped superconducting compound. Magnetic order of the transition-metal sub-lattice (V or Cr) in the perovskite layer does not seem to alter essential features of the FeAs layers, similarly to the case of the ordering of the rare-earth moments in the 1111 systems. The quasi two-dimensional feature of the 42622 systems seems to work against static antiferromagnetic

order of the Fe moments. This suppression of competing magnetic order might provide an indirect effect for promoting superconductivity in various perov-FeAs systems and lead to rather high T_c 's of newly discovered homologous systems which have FeAs interlayer distances even larger than those of the 42622 systems.

Acknowledgement: This work has been supported by the US NSF under the Materials World Network (MWN: DMR-0502706 and 0806846) and the Partnership for International Research and education (PIRE: OISE-0968226) programs at Columbia, by Canadian NSERC and CIFAR at McMaster, and by CNPq and Faperj at CBPF in Rio, Brazil and NSFC and MOST of China: 973 project 2011CB605900 at IOP in Beijing.

* author to whom correspondences should be addressed:
E-mail tomo@lorentz.phys.columbia.edu

- [1] Y. Kamihara *et al.*, J. Amer. Chem. Soc. **130** (2008) 3296.
- [2] X.H. Chen *et al.*, Nature **453** (2008) 761; G.F. Chen *et al.*, Phys. Rev. Lett. **100** (2008) 247002; Zhi-An Ren *et al.*, Europhys. Lett. **83** (2008) 17002. H.H. Wen *et al.*, Europhys. Lett. **82** (2008) 17009.
- [3] C. de la Cruz *et al.*, Nature **453** (2008) 899.
- [4] J. Zhao *et al.*, Natur. Mater. **7** (2008) 935.
- [5] H. Luetkens *et al.*, Natur. Mater. **8** (2009) 305; A.J. Drew *et al.*, Natur. Mater. **8** (2009) 310.
- [6] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101** (2008) 107006; G.F. Chen *et al.*, Chin. Phys. Lett. **25** (2008) 3403.
- [7] M.S. Torikachvili, S.L. Bud'ko, N. Ni, P.C. Canfield, Phys. Rev. Lett. **101** (2008) 057006.
- [8] P.L. Alireza *et al.*, J. Phys.: Condens. Matter **21** (2009) 012208.
- [9] S.C. Wang *et al.*, Solid State Commun. **148** (2008) 538.
- [10] D.R. Parker *et al.*, Phys. Rev. Lett. **104** (2010) 057007.
- [11] H. Ogino, Y. Katsura, S. Horii, K. Kishio, J. Shimoyama, Supercond. Sci. Technol. **22** (2009) 085001
- [12] X. Zhu *et al.*, Phys. Rev. **B 79** (2009) 220512(R)
- [13] F. Han *et al.*, Sci China Ser G, **53** (2010) 1202.
- [14] M. Tegel *et al.*, Europhys. Lett. **89** (2010) 37006.
- [15] M. Tegel, I. Schellenberg, F. Hummel, R. Poettgen, D. Johrendt, Z. Naturforsch. B - Chem. Sci. **64B** (2009) 815.
- [16] H. Kotegawa *et al.*, arXiv:1009.5491v1.
- [17] H. Ogino *et al.*, Supercond. Sci. Technol. **23** (2010) 115005.
- [18] M. Tegel *et al.*, Z. Anorg. Allg. Chem. **635** (2009) 2242.
- [19] M. Tegel *et al.*, arXiv:1008.2687v2.
- [20] G. Cao *et al.*, Phys. Rev. **B82** (2010) 104518.
- [21] Y.J. Uemura, Physica **B404** (2009) 3195.
- [22] K.M. Kojima *et al.*, Phys. Rev. Lett. **78** (1997) 1787.
- [23] L.P. Le *et al.*, Phys. Rev. Lett. **68** (1992) 1923.
- [24] I.I. Mazin, Phys. Rev. **B81** (2010) 020507(R).
- [25] K.W. Lee and W.E. Pickett, Euro Phys. Lett. **89** (2010) 57008.